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FULL CONTENTS CLAIM + DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

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FULL CONTENTS

[Claim(s)]

[Claim 1] The zirconia sheet which consists of a sheet-like zirconia sintered compact and is characterized by for each surface roughness of sheet both sides being 0.3-3 micrometers in a maximum height (Ry), and being 0.02-0.3 micrometer in arithmetic mean roughness (Ra).

[Claim 2] The zirconia sheet according to claim 1 which the surface roughness ratios of an other side side (field with the smaller above Ry and Ra) of a sheet which, on the other hand, receive a side face (field with the smaller above Ry and Ra) are 1-5 in a maximum height ratio (Ry ratio), and are 1-10 in an arithmetic-mean-roughness ratio (Ra ratio).

[Claim 3] The zirconia sheet according to claim 1 or 2 which is what a zirconia sintered compact becomes from the zirconium oxide stabilized with 2-7mol% of yttrium oxide.

[Claim 4] The zirconia sheet according to claim 1 to 3 which is what is used as a solid-electrolyte membrane.

[Claim 5] As slurry used for manufacture of a green sheet, the mean particle diameter (diameter of 50 volume %) of a formed element 0.05-0.8 micrometer, The process of the zirconia sheet characterized by sintering after using the slurry whose diameter of 90 volume % is 0.5-2 micrometers, and whose marginal particle diameter (diameter of 100

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volume %) is 5 micrometers or less and fabricating this in the shape of a sheet.
[Claim 6] The process according to claim 5 which manufactures the zirconia sheet which satisfies requirements according to claim 1 to 4.

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Especially this invention relates to the zirconia sheet improved so that the adhesion of a sheet and an electrode can be raised, and its process, when performing electrode formation to both sides by screen-stencil etc. about a zirconia sheet and its process.
[0002]
[Description of the Prior Art] Since Ceramics Sub-Division is excellent in electric and magnetic characteristics etc. in addition to mechanical properties, such as a heat-resisting property and abrasion resistance, it is utilized in many fields. Since it has oxygen ion conductivity, heat resistance and corrosion resistance, the outstanding toughness, outstanding chemical resistance, etc., the ceramic sheet which makes zirconia a subject especially is utilized as the solid-electrolyte membrane of the sensor components like an oxygen sensor or a humidity sensor, a solid-electrolyte membrane further for fuel cells, etc.
[0003] By the way, the general processes of a zirconia sheet are a doctor blade method, the calender method, an extruding method, etc. about the slurry which consists of the end of zirconia precursor powder, an organic matter binder, and a dispersion medium. While fabricate in the shape of a sheet, dry this, volatilize a dispersion medium and a green sheet is obtained, it calcinates after arranging this with suitable size by a cut, punching, etc., and carrying out decomposition clearance of the organic matter binder, it is the method of making ceramic powder sintering mutually.
[0004] On the other hand, when you put a zirconia sheet in practical use as an object for the solid-electrolyte membranes of a fuel cell, perform electrode printing to both sides of this sheet by screen-stencil etc. A fuel electrode and an oxygen pole are formed, and since it is laminated and attached to a separator, INTAKONEKUTA, etc. and a multilayer, big lamination load is added also to the electrode formed in both sides of a solid-electrolyte membrane. Moreover, since it is put to the elevated temperature of 800-1000 degrees C at the time of operation, if an electrode layer exfoliates easily from a zirconia sheet and it is in charge of manufacture of a solid-electrolyte membrane with few [the coefficient of thermal expansion of a zirconia sheet and an electrode layer] differences, the adhesion of the electrode to a zirconia sheet becomes very important.
[0005] That is, when the adhesion to this zirconia sheet of the electrode formed in both sides of a zirconia sheet of screen-stencil etc. runs short, when putting in practical use as a fuel cell, this electrode produces exfoliation, omission, etc. from a zirconia sheet, and the engine

performance as a fuel cell falls rapidly, and results impossible [operation]. In the zirconia sheet which follows, for example, is used as an object for the solid-electrolyte membranes of a fuel cell etc., it becomes very important, when planning the life extension as a fuel cell to raise adhesion with the electrode by which printing formation is carried out.

[0006] Then, with a screen-stencil technique, it is that the problem of the above electrode exfoliations should be prevented as much as possible, With printing or a coating method, precede carrying out for electrode formation and [degreasing treatment] In order to raise adhesion of the ink to impression papers, such as a ceramics sheet, a PET film, an acrylic plate, and an aluminum plate, Although it is pretreating performing corona discharge treatment, flame treatment, and anchor treatment (formation of the thin paint film by RABIA coating) to the surface, or carrying out surface roughening of the surface etc., such pretreatment is complicated, requires trouble and becomes the cause of reducing productivity substantially.

[0007] The problem of the adhesion of the electrode to such a zirconia sheet etc. becomes very important also in thick film boards and thin film boards, such as not only the solid-electrolyte membrane for fuel cells but a hybrid IC, a solid-electrolyte membrane, a sensor base for sensors, etc.

[0008]

[Problem(s) to be Solved by the Invention] This invention is made paying attention to the above situations, and [the object] It is in offering the technique which can join electrode printing etc. to the surface powerfully with high adhesion for the nature [of as / whose gas permeability is zero substantially / which is 97% or more] zirconia sheet of precise with which electrode printing etc. is performed to both sides like the object for solid-electrolyte membranes.

[0009]

[Means for Solving the Problem] [sheet / concerning this invention which was able to solve the above-mentioned technical problem / zirconia] It consists of a sheet-like zirconia sintered compact, and each surface roughness of sheet both sides has a summary at the place which is 0.3-3 micrometers in a maximum height (Ry), and is 0.02-0.3 micrometer in arithmetic mean roughness (Ra).

[0010] In the above-mentioned zirconia sheet of this invention, it adds to the maximum height (Ry) and arithmetic mean roughness (Ra) of a field of above-mentioned each. [the surface roughness ratio of an other side side (field with the smaller above Ry and Ra) of this sheet which, on the other hand, receives a side face (field with the smaller above Ry and Ra)] Since what is 1-10 in 1-5, and an arithmetic-mean-roughness ratio (Ra ratio) can give advanced adhesion to both sides and can control much more effectively exfoliation of the electrode coat at the time of operation etc., it is desirable at a maximum height ratio (Ry ratio).

[0011] Moreover, 10 micrometers or more of the thickness [30 micrometers or more of] is 50 micrometers or more still more preferably more preferably, and 200 micrometers or less are especially preferably desirable [this zirconia sheet] from the meaning which raises the

practicability as a solid-electrolyte membrane etc., 300 micrometers or less more preferably 500 micrometers or less. As desirable zirconia which constitutes this sheet Rare earth element oxides, such as alkaline earth metal oxides, such as MgO, CaO, SrO, and BaO, Y2O3, La2O3, CeO2, Pr2O3, Nd2O3, Sm2O3, Eu2O3, Gd2O3, Tb2O3, Dy2O3, Ho2O3, Er2O3, and Yb2O3, One sort or the zirconia contained two or more sorts may be mentioned in the stabilizing agent of Sc2O3, Bi2O3, and In2O3 grade, and SiO2, Al2O3, germanium2O3, B-2 O3, SnO2, Ta2O5, and Nb2O5 grade may be contained as other additives.
[0012] especially when [more advanced] securing thermal, mechanical, electric, and chemical property The zirconium oxide of right **** stabilized with 2-7mol% of yttrium oxide and/or a cubic configuration is desirable, and this zirconia sheet can be utilized especially very effectively as an object for the solid-electrolyte membranes of a fuel cell also in the object for solid-electrolyte membranes.
[0013] And the process of this invention offers the method that the zirconia sheet which fulfills the above surface descriptions can be obtained certainly, and [the architecture] As slurry used for manufacture of a green sheet, the mean particle diameter (diameter of 50 volume %) of a slurry formed element 0.05-0.8 micrometer, The slurry whose diameter of 90 volume % is 0.5-2 micrometers and whose marginal particle diameter (diameter of 100 volume %) is 5 micrometers or less is used, and it has a summary at the place sintered after fabricating this in the shape of a sheet.
[0014]
[Embodiment of the Invention] Under a settlement technical problem which was mentioned above, this invention persons have advanced investigation to both sides of a zirconia sheet wholeheartedly that formation of electrode printing etc. with high adhesion should be made possible. As a result, for the improvement in adhesion, the surface roughness of these sheet both sides is very important, and what adjusted the surface roughness so that it might become specific within the limits by maximum roughness (Ry) and arithmetic mean roughness (Ra) knows that adhesion with electrode printing etc. will be raised certainly, and hits on an idea of it to above-mentioned this invention.
[0015] Namely, when applying or coating a zirconia sheet with an electrode by screen-stencil etc., in order to raise the adhesion of this sheet and electrode printing It was checked that it is required to make surface roughness of these sheet both sides into the proper range, this surface roughness shows 0.3-3 micrometers with a maximum height (Ry), and the thing within the limits of 0.02-0.3 micrometer shows high adhesion by the interface of a sheet surface and an electrode printing layer by arithmetic mean roughness (Ra).
[0016] Namely, [Ry / when less than 0.3 micrometer and/or Ra are less than 0.02 micrometers, line width and pitch can put in practical use convenient as a high-density wiring board used at a room temperature narrowly and substantially, but] specifically when this sheet surface is too smooth When it is put at an elevated temperature for a long time on the occasion of the time of sintering after electrode formation, or an

activity, or when a heat history is repeatedly received between a room temperature and an elevated temperature, it is easy to cause exfoliation between the sheet surface and an electrode surface. Therefore, in order to avoid such a problem, in advance of spreading formation of an electrode, a complicated surface roughening process etc. is needed. However, when Ry specifically exceeds 3 micrometers when the surface roughness of this sheet is too large, and/or Ra exceeds 0.3 micrometer, electrode formation of uniform thickness becomes difficult and the adhesion of a zirconia sheet falls further.

[0017] [being adopted generally as a method of incidentally fabricating a zirconia sheet] [the slurry which consists of the end of zirconia precursor powder, an organic matter binder and a dispersion medium like the above-mentioned] By the doctor blade method, the calender method, an extruding method, etc., cover on a support plate or a carrier film, spread, and it fabricates in the shape of a sheet. Dry this, volatilize a dispersion medium, obtain a green sheet, and this is cut. It is the method of making ceramic powder sintering mutually while it calcinates after keeping step with suitable size by punching etc., and carrying out decomposition clearance of the organic matter binder. The surface side wide opened by the air at the time of desiccation tends to become a roughened surface rather than the field which touched the carrier film while the field which touched the above-mentioned support plate and the carrier film becomes smooth Since it is required in this invention to give the electrode adhesion excellent in both sides of this film, it has specified so that it may be settled within limits which each double-sided surface roughness mentioned above.

[0018] In addition, JIS revised in 1994 with the above-mentioned surface roughness as used in the field of this invention Saying the value measured based on B-0601, the used measuring instrument is the TOKYO SEIMITSU CO. LTD. "surfboard COM 1400A."

[0019] namely, the case where Ry is measured -- Ry -- 0.3 micrometer -- super- -- when it is the range which is 0.5 micrometer, it measures by basis length l being 0.25mm, it setting assessment length ln to 1.25mm, and Ry exceeding 0.5 micrometer, and the case of less than three setting basis length l to 0.8mm, and setting assessment length ln to 4mm.

[0020] Moreover, in measurement of Ra, Ra exceeds 0.02 micrometer and it [in the case of 0.1 micrometer or less] Cut-off value lambdac shall be 0.25mm, the assessment length ln shall be 1.25mm, Ra exceeds 0.1 micrometer, and, in the case of 0.3 micrometer or less, it is the value which measured 0.8mm and the assessment length ln for cut-off value lambdac as 4mm.

[0021] [and the thing to which the surface roughness of sheet both sides called for by this method is restored to the above-mentioned range] Also in the time of the operation which can secure the adhesion of a height level and is put to the time of electrode calcination, or an elevated temperature by the moderate anchor effect while being able to carry out the spreading formation of the electrode of thickness uniform to both sides of a sheet easily Moreover, even when the heat history repeatedly put to hot conditions is received from low temperature, it becomes

possible to prevent exfoliation of an electrode coat as much as possible.
[0022] In consideration of the both sides of the formation nature of the above-mentioned electrode coat, and adhesion, 0.35 micrometers or more of more desirable surface roughness is 0.5 micrometers or more more preferably in Ry, and 2 micrometers or less are 0.025 micrometers or more and 0.1 micrometer or less in 1.5 micrometers or less and Ra more preferably.
[0023] When using a zirconia sheet as an electrolyte membrane, an electrode will not be in the minute condition that circuit formation is carried out with fine line width like the conductor of the electronic industry material board like a hybrid IC, fundamentally. the sheet except the seal part of the sheet periphery part -- since it is mostly made the whole surface with ** As a factor of surface roughness, the Ry is more important than Ra, and even when it is repeatedly put to the temperature region to ordinary temperature - the elevated temperature near 1000 degree C by making especially Ry into the range of 0.3-3 micrometers, exfoliation with a zirconia sheet and an electrode layer covers a long time, and becomes difficult to take place.
[0024] Moreover, in order to enable formation of an electrode coat with high adhesion in this invention at sheet both sides, The surface roughness ratios of an other side side (field with the smaller above Ry and Ra) of a sheet which, on the other hand, receive a side face (field with the smaller above Ry and Ra) are 1 or more and 4 or less more preferably five or less one or more in a maximum height ratio (Ry ratio). And it is [one or more / ten or less] desirable at an arithmetic-mean-roughness ratio (Ra ratio) to make it more desirable within the limits of 1 or more and 5 or less.
[0025] When the above-mentioned Ry ratio and Ra ratio incidentally exceed the above-mentioned optimum range, since double-sided surface roughness is too different, exfoliation of a zirconia sheet and an electrode layer takes place easily intensively in the one where printability or adhesion is worse, and the quality as the whole goods becomes inferior.
[0026] The process in particular of the zirconia sheet which fills the above-mentioned surface roughness is not restricted, but according to a conventional method The end of zirconia precursor powder, the quality of organicity or a minerals binder, and a dispersion medium (solvent), The slurry which contains a dispersant, a plasticizer, etc. as occasion demands A doctor blade method, It applies by thickness suitable on a smooth substrate, for example, a polyester sheet, by the calendering roll method, an extruding method, etc. After obtaining a green sheet and cutting this in suitable magnitude by drying and carrying out volatilization clearance of the dispersant, the method of laying in the porosity setter on a shelf board, and carrying out heating calcination at the temperature of about 1400-1600 degrees C for about 2 to 5 hours is adopted.
[0027] At this time, the grain size architecture in the end of zirconia precursor powder affects the surface roughness of a completion sheet most, if a coarser thing is used, surface roughness will become coarse relatively, and if a detailed thing is used, surface roughness will become

small relatively. And in order to obtain more efficiently the zirconia sheet of said surface roughness range meant by this invention It is desirable to use that (small thing of particle size distribution) to which it is the range whose mean particle diameter is 0.1-0.8 micrometer as the end of precursor powder it is used, and the grain size was equal as much as possible, and the thing more than whose 90 volume % of these fine particles is specifically 5 micrometers or less.

[0028] however, [in the place where this invention persons repeated investigation further] [that it is more important when securing the above-mentioned surface roughness specified by this invention] It is the grain size architecture of the formed element contained in said slurry at the time of coating in the end of precursor powder it mentioned above the shape of not grain size architecture but a sheet of the very thing. If this grain size architecture uses the slurry which satisfies the requirements for 5 micrometeror less ** by 0.05 micrometers or more, 0.5 micrometer or less, and the diameter of 90 volume % with 0.5 micrometers or more, 2 micrometers or less, and marginal particle diameter (diameter of 100 volume %) with mean particle diameter (diameter of 50 volume %) It is checking that the zirconia sheet which satisfies the requirements for said surface roughness more certainly is obtained.

[0029] The more desirable grain size architecture of the formed element contained in the above-mentioned slurry is [in mean particle diameter (diameter of 50 volume %) / in 0.1 micrometers or more, 0.5 micrometer or less, and the diameter of 90 volume %] 3 micrometers or less at 0.8 micrometers or more, 1.5 micrometers or less, and marginal particle diameter (diameter of 100 volume %).

[0030] Although the method of carrying out kneading crushing uniformly, covering the suspension of said raw material combination including the end of precursor powder over a ball mill etc. in preparation of the above-mentioned slurry incidentally is adopted Since a part of end of precursor powder causes secondary condensation at these slurry preparation processes depending on these kneading conditions (the class of dispersant, the addition of a dispersant, etc. are included) or a portion is crushed further, the grain size architecture in the end of precursor powder does not necessarily become the same as the grain size architecture of the formed element in slurry as it is. Therefore, when manufacturing the zirconia sheet of this invention, it can be called a method with more positive adjusting so that the grain size architecture of the formed element contained in slurry before coating in the shape of a sheet as a factor which has on the surface roughness of this sheet most may become in the above-mentioned optimum range.

[0031] In addition, the value which measured the grain size architecture of the formed element in the above-mentioned end of precursor powder and slurry by the following method is said. Namely, the grain size architecture in the end of precursor powder uses the Shimadzu laser diffraction type particle-size-distribution measuring apparatus "SALD-1100", and the aqueous solution which added 0.2weight % of sodium metaphosphate as a dispersant in distilled water is made into a dispersion

medium. Are the measured value after having added 0.01 to 1 weight % into these 100 cc of dispersion media in the end of precursor powder, ultrasonicating for 1 minute and making it distribute, and [moreover, the grain size architecture of the formed element in slurry] It is the measured value after using the solvent in slurry, and the solvent of this presentation as a dispersion medium, ultrasonicating each slurry for 1 minute similarly in addition and distributing it in these 100 cc of dispersion media so that it may become 0.01 to 1 weight %.

[0032] [even if the zirconia sheet of this invention consists only of zirconium oxide substantially, of course, do not care about it, but] For example, since thermal, mechanical, electric, and the chemical property of altitude are required more of the sheet used as an object for the solid-electrolyte membranes of a fuel cell etc., in order to satisfy such demand characteristics It is recommended as what [2-7mol / % and what has more desirable and more desirable 2.5-6mol % and the zirconium oxide (right **** and/or cubic zirconia) stabilized still more preferably with 3.5-5mol% of yttrium oxide].

[0033] Moreover, when putting this especially zirconia sheet in practical use as an object for the solid-electrolyte membranes of a fuel cell, in order to stop energization Ross as much as possible, filling claim hardness, it is good to be 50 micrometers or more more preferably and for 10 micrometers or more of sheet thickness [500 micrometers or less of] to be 300 micrometers or less more preferably.

[0034] Moreover, as a configuration of a sheet, any are sufficient as circular, an ellipse form, a square shape with R (R), etc., and you may have holes, such as circular [same in these sheets], an ellipse form, and a square shape with R. Furthermore, the area of a sheet is 100cm2 or more preferably 50cm2 or more. In addition, this area means the area of the periphery edge having contained the area of this hole, when a hole is in a sheet.

[0035] There is no exceptional restraint also in the class of binder used by this invention, and the binder of the quality of organicity or minerals known from the former can be used, choosing it suitably. As an organic matter binder, for example An ethylene system copolymer, a styrene system copolymer, Cellulose, such as an acrylate system and a methacrylate system copolymer, a vinyl acetate system copolymer, a maleic acid system copolymer, vinyl butyral system resin, vinyl acetal system resin, vinyl formal system resin, vinyl alcohol system resin, waxes, and ethyl cellulose, is illustrated.

[0036] Also in these, [points /, such as the moldability of a green sheet, and hardness, pyrolysis nature at the time of calcination,] Methyl acrylate, ethyl acrylate, propylacrylate, Butyl acrylate, isobutyl acrylate, cyclohexyl acrylate, The alkyl acrylate which has a with a carbon numbers [, such as 2-ethylhexyl acrylate,] of ten or less alkyl group And methyl methacrylate, ethyl methacrylate, butyl methacrylate, Isobutyl methacrylate, octyl methacrylate, 2-ethylhexyl methacrylate, DESHIRU methacrylate, dodecyl methacrylate, lauryl methacrylate, The alkyl methacrylate which has a with a carbon numbers [, such as cyclohexyl methacrylate,] of 20 or less alkyl group Hydroxyethyl acrylate,

hydroxypropyl acrylate, The hydroxyalkyl acrylate or hydroxyalkyl methacrylate which has hydroxyalkyl machines, such as hydroxyethyl methacrylate and hydroxypropyl methacrylate, Amino alkyl acrylate or amino alkyl methacrylate, such as dimethylamino ethyl acrylate and dimethylaminoethyl methacrylate, (Meta) Obtain at least one sort of carboxyl group inclusion monomers, such as maleic acid half ester like acrylic acid, maleic acid, and mono-isopropyl malate, a polymerization or by carrying out copolymerization. A number average molecular weight is recommended as 20,000-200,000, and a more desirable thing that has the desirable acrylate (meta) system copolymer of 50,000-100,000. These organic matter binders can be used independently, and also they can be used as occasion demands, combining two or more sorts suitably. Especially a desirable thing is the polymer of the monomer which contains isobutyl methacrylate and/or 2-ethylhexyl methacrylate 60weight % or more.

[0037] Moreover, as a minerals binder, zirconia sol, silica sol, alumina sol, titania sol, etc. are independent, or can mix and use two or more sorts.

[0038] [the rate of an use rate of the end of zirconia precursor powder, and a binder] To a former 100 weight part, the latter 5 - 30 weight parts, and when the range of 10 - 20 weight part is more preferably suitable and the amount of the binder used runs short The hardness and the plasticity of a green sheet become inadequate, when too conversely large, viscosity adjustment of slurry not only becomes difficult, but decomposition bleedoff of the binder component at the time of calcination becomes mostly and intense, and a homogeneous sheet becomes is hard to be obtained.

[0039] moreover, as a solvent used for manufacture of a green sheet Water, methanol, ethanol, 2-propanol, 1-butanol, Ketone, such as alcohols, such as 1-hexanol, acetone, and 2-butanone, They are used acetate's, such as aromatic hydrocarbon's, such as aliphatic hydrocarbon's, such as pentane's, hexane's, and heptane's, benzene's, toluene's, xylene's, and ethylbenzene's, methyl acetate's, ethyl acetate's, and butyl acetate's, choosing suitably. These solvents can also be used independently and also two or more sorts can be used, mixing suitably. The amount of these solvents used is good for slurry viscosity to adjust 10-200poise often [considering the viscosity of slurry at the time of green sheet shaping, and adjusting suitably], and preferably, so that it may become the range of 10-50poise more preferably.

[0040] In order to promote amalgam decomposition and dispersion in the end of zirconia precursor powder in preparation of the above-mentioned slurry, Polyelectrolyte, such as polyacrylic acid and polyacrylic acid ammonium, citric acid, The copolymer and its ammonium salt, or amine salt of an organic acid, isobutylene or styrene, and maleic anhydride, such as tartaric acid, The dispersant which consists of a copolymer, its ammonium salt, etc. of butadiene and maleic anhydride; Dibutyl phtalate for giving plasticity to a green sheet, The plasticizer which consists of glycols and glycol ether, such as phthalic ester, such as dioctyl phthalate, and propylene glycol; a surface active agent, a defoaming agent, etc. can

be added further if needed.
[0041] After fabricating the slurry which consists of the above-mentioned raw material combination by the above methods in the shape of a sheet, drying and obtaining a zirconia green sheet, the zirconia sheet of this invention is obtained by carrying out heating calcination of this. As a means for obtaining a ceramics sheet with high flatness in this baking process, without producing camber and a wave Contraction by heating until it has the area more than this green sheet and results in the burning temperature of this green sheet [5% or less] And the thing from which the periphery does not protrude said green sheet between the porous sheets which have 5 to 60% of bulk density to theoretical density, from which it puts like, and calcinates, or the periphery of said green sheet does not protrude the above-mentioned porous sheet and which is calcinated after carrying like is desirable.
[0042]
[Example] Although a work example and a comparative example are given and this invention is explained more concretely hereafter, this invention does not receive a restraint according to the following work example from the first, it is also possible to change suitably and to carry out in the range which may suit before and the after-mentioned meaning, and each of they is included by the technical range of this invention.
[0043] 3 mol % yttria-stabilized-zirconia powder of work-example 1 marketing (as the binder (molecular weight: 30000, glass-transition-temperature:-8 degree C) 15 weight part which consists of an methacrylic system copolymer to a trade name "HSY-3.0" by first rare element company 100 weight part, and a plasticizer) The partially aromatic solvent 50 weight part of toluene/isopropanol (bulk density = 3/2) was put into the nylon pot in which the zirconia ball 5mm in diameter was inserted as a dibutyl phthalate 2 weight part and a dispersion medium, it kneaded at 70% of about 60rpm of critical velocity for 40 hours, and slurry was prepared.
[0044] A part of this slurry is extracted and it dilutes with the partially aromatic solvent of toluene/isopropanol (bulk density = 3/2). When the particle size distribution of the formed element in slurry was measured using the Shimadzu particle-size-distribution measuring apparatus "SALD-1000", it was checked that 0.35 micrometer and the diameter of 90 volume % are [0.85 micrometer and the marginal particle diameter (diameter of 100 volume %) of mean particle diameter (diameter of 50 volume %)] 1.95 micrometers.
[0045] After carrying out concentration degassing of this slurry, adjusting viscosity to 30poise (23 degrees C) and letting it pass in the filter of 200 meshes finally, it coated on the polyethylene terephthalate (PET) sheet with the doctor blade method, and the green sheet was obtained. This green sheet was cut for the square, after inserting those upper and lower sides with the 99.5% alumina porosity plate (porosity: 30%) whose swell maximum height is 10 micrometers and degreasing, heating calcination was carried out at 1480 degrees C for 3 hours, and the 3 mol % yttria-stabilized-zirconia sheet with an about 100mm angle and a thickness of 0.1mm was obtained.

[0046] A field with the gloss in contact with the PET film of the obtained green sheet (PET side), The field (Air side) put to the air by the side of opposite [the] was equally divided into 100 at the 10mm angle, respectively, and surface roughness was measured at 0.30mm/sec in measurement velocity about the parting plane of both sides 200 using the surface roughness meter by Tokyo Seimitsu Co., Ltd. "surfboard COM 1400A" in total. In addition, JIS revised in the solution parameter in measurement in 1994 Normal of B-0601 was applied. A result is shown in Table 1.

[0047] Slurry was prepared completely like the above-mentioned work example 1 except having replaced the end of work-example 2 zirconia precursor powder with commercial 4.5 mol % yttria-stabilized-zirconia powder (trade name by the first rare element company "HSY-4.5"). When this a part of slurry was extracted and the particle size distribution of the formed element was measured by the same method as the above-mentioned work example, it was checked that 0.28 micrometer and the diameter of 90 volume % are [0.79 micrometer and the marginal particle diameter of mean particle diameter] 1.54 micrometers.

[0048] This slurry was used, the 4.5 mol % yttria-stabilized-zirconia sheet of the about 100mm angle (about 0.2mm in thickness) was manufactured like the above, and surface roughness was measured similarly.

[0049] Slurry was prepared completely like the above-mentioned work example 1 except having replaced the end of work-example 3 zirconia precursor powder with commercial 6 mol % yttria-stabilized-zirconia powder (trade name by the first rare element company "HSY-6.0"). When this a part of slurry was extracted and the particle size distribution of the formed element was measured by the same method as the above-mentioned work example 1, it was checked that 0.43 micrometer and the diameter of 90 volume % are [1.65 micrometers and the marginal particle diameter of mean particle diameter] 2.21 micrometers.

[0050] This slurry was used, the 6 mol % yttria-stabilized-zirconia sheet 100mm in diameter (about 0.25mm in thickness) was manufactured like the above, and surface roughness was measured similarly.

[0051] Except having replaced with in the end of work-example 4 zirconia precursor powder, and having used the mixed powder end of a commercial 8 mol % yttria-stabilized-zirconia powder (trade name by first rare element company "HSY-8.0") 100 weight part and a commercial high-purity-alumina powder (trade name by Daimei Telecom Engineering chemistry company "TMDAR") 0.5 weight part Make it be completely the same as that of said work example 1. Slurry was prepared. When this a part of slurry was extracted and the particle size distribution of the formed element was measured by the same method as the above-mentioned work example 1, it was checked that 0.12 micrometer and the diameter of 90 volume % are [0.88 micrometer and the marginal particle diameter of mean particle diameter] 2.1 micrometers.

[0052] This slurry was used, the 8 mol % yttria-stabilized-zirconia sheet 100mm in diameter (about 0.3mm in thickness) was manufactured like

the above, and surface roughness was measured similarly.
[0053] The same slurry raw material as having used in the comparative example 1 above-mentioned work example 1 was paid in the nylon pot in which the Nylon ball 15mm in diameter was inserted, it kneaded at 50% of about 40rpm of critical velocity for 40 hours, and slurry for green sheet shaping was prepared. When this a part of slurry was extracted and the particle size distribution of the formed element was measured by the same method as the above-mentioned work example, it was checked that 0.71 micrometer and the diameter of 90 volume % are [1.96 micrometers and the marginal particle diameter (diameter of 100 volume %) of mean particle diameter (diameter of 50 volume %)] 3.68 micrometers.
[0054] This slurry was used, the 3 mol % yttria-stabilized-zirconia sheet of the about 100mm angle (about 0.1mm in thickness) was manufactured like the above, and surface roughness was measured similarly.
[0055] To a comparative example 26 mol % yttria-stabilized-zirconia powder (before said) 100 weight part, it is a dispersion medium. The sorbitan acid 1 weight part was added as a dispersant with toluene / isopropanol (3/2) partially aromatic solvent 50 weight part, and it mixed like said work example 1 using the ball mill which inserted in the zirconia ball 3mm in diameter. Subsequently, the dibutyl phthalate 2 weight part was added as a plasticizer with the binder 15 weight part which consists of a methacrylic acid system copolymer, it kneaded with the ball mill further for 20 hours, and slurry for green sheet shaping was prepared. When this a part of slurry was extracted and the particle size distribution of the formed element was measured by the same method as the above-mentioned work example, as for 0.48 micrometer and marginal particle diameter, as for mean particle diameter, it was checked that 0.10 micrometer and the diameter of 90 volume % are 1.75 micrometers.
[0056] This slurry was used, the 6 mol % yttria-stabilized-zirconia sheet 100mm in diameter (about 0.3mm in thickness) was manufactured like the above-mentioned work example 3, and surface roughness was measured similarly.
[0057] [Performance evaluation test] It is an electrode to the both sides after **(ing) each zirconia sheet obtained by the above-mentioned work examples 1-4 and comparative examples 1 and 2 in a sodium hydroxide aqueous solution 5%, applying a supersonic wave for 3 minutes and degreasing the sheet surface, The nickel oxide powder / zirconium oxide powder inclusion paste with which both zirconia sheets and coefficients of thermal expansion were doubled are screen-stenciled to one field. after drying at 100 degrees C, heating calcination was carried out at 1300 degrees C for 1 hour, subsequently, on the other hand, the lanthanum strontium comics NETO (La0.8Sr0.2MnO3) powder inclusion paste was boiled, and was screen-stenciled, it calcinated at 1000 degrees C for 1 hour, and the zirconia sheet with a double-sided electrode was obtained.
[0058] While carrying out visual observation of the surface description of each obtained sheet, SEM photograph observation of the interface of the electrode printing layer in each sheet was carried out, and visual

evaluation of the interface description was carried out. A result is shown in Table 2. In addition, in Table 1, the grain size architecture of the formed element in the slurry used for manufacture of each zirconia sheet was also written together.

[0059]

[Table 1]

		実施例1	実施例2	実施例3	実施例4	比較例1	比較例2
Ry	最大値	1.1	2.6	0.9	0.8	3.7	0.4
	平均値	0.7	1.5	0.6	0.5	2.4	0.2
	最小値	0.5	1.1	0.4	0.3	1.3	0.08
Ra	最大値	0.08	0.16	0.08	0.06	0.5	0.02
	平均値	0.05	0.1	0.04	0.03	0.4	0.01
	最小値	0.04	0.07	0.03	0.02	0.1	0.008
粒度分布（μm）平均径		0.35	0.28	0.43	0.12	0.71	0.1
90体積%径		0.85	0.79	1.65	0.88	1.96	0.48
限界粒子径		1.95	1.54	2.21	2.1	3.68	1.75

[0060]

[Table 2]

	実施例1	実施例2	実施例3	実施例4	比較例1	比較例2
シート・電極の界面状態	密着	密着	密着	密着	一部剥離	剥離
電極層の厚さの状態	厚さ均一	厚さほぼ均一	厚さほぼ均一	厚さほぼ均一	不均一	厚さ均一

[0061] In the work examples 1-4 by which the surface roughness of zirconia sheet both sides satisfies the requirements for normal of this invention so that clearly also from Tables 1 and 2 To all having the thickness in which the surface description of a sheet is good and almost uniform, and the adhesion of a sheet and an electrode being also excellent when the surface roughness by the side of a sheet piece side is too coarse (comparative example 1) Although surface description is uneven, partial exfoliation of an electrode is seen and the thing of thickness good [the surface description of a sheet] and uniform is obtained in the case (comparative example 2) of being too smooth, adhesion with an electrode has produced exfoliation bad.

[0062]

[Effect of the Invention] By consisting of this inventions as mentioned above, and specifying the surface roughness of zirconia sheet both sides Even when performing electrode printing to both sides like the object for solid-electrolyte membranes, this electrode can be powerfully joined with advanced adhesion, without producing which problem with local poor energization by the thickness heterogeneity of this electrode printing. The partial exfoliation at the time of electrode formation and exfoliation of the electrode at the time of operation can be controlled as much as possible, and it uses especially as an object for fuel cells. Therefore, power generation characteristics and endurance of a fuel cell are substantially extensible.

[Translation done.]

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